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Bis(tetraphenylphosphonium) bis(1-carboxybenzene-2,3-diolato-kappa O-2,O ')-cis-dioxomolybdate(VI)

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akaraliota@chem.uoa.gr**Key indicators**

Single-crystal X-ray study

T = 150 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.045

wR factor = 0.100

Data-to-parameter ratio = 22.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**Bis(tetraphenylphosphonium) bis(1-carboxybenzene-2,3-diolato- $\kappa^2\text{O},\text{O}'$)-cis-dioxomolybdate(VI)**

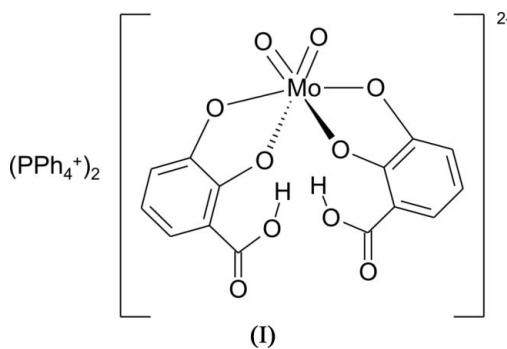
The title compound, $(\text{C}_{24}\text{H}_{20}\text{P})_2[\text{Mo}(\text{C}_7\text{H}_4\text{O}_4)_2\text{O}_2]$, contains a distorted octahedral molybdenum(VI) complex having the characteristic *cis*- MoO_2^{2+} group and the ligand 2,3-dihydroxybenzoic acid coordinated through the two phenolate O atoms, while the carboxyl group is not deprotonated. No π - π overlap between the benzene rings of the ligands or those of the tetraphenylphosphonium ions is observed.

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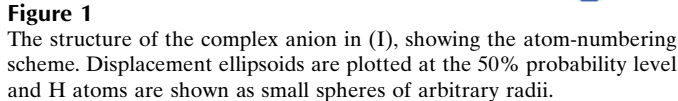
Comment

The title compound, (I), results from the reaction of a mixture of tetraphenylphosphonium bromide (PPh_4Br), 2,3-dihydroxybenzoic acid (2,3-DHBA) and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in an aqueous solution (pH 6) with subsequent redissolution of the precipitate in dichloromethane. This method of preparation differs from that reported for the same metal-organic anion in $(\text{NMe}_4)_2\text{MoO}_2(\text{C}_7\text{H}_4\text{O}_4)_2 \cdot 1.5\text{H}_2\text{O}$, (II) (Griffith *et al.*, 1995), and is less complicated. At lower pH values, the formation of oligomeric molybdenum complexes is preferred due to the presence of the ligand in its semi-oxidized form (semiquinone), which promotes oligomerization (Lymberopoulou-Karaliota *et al.*, 2005; Karaliota *et al.*, 2002).



In the complex anion of (I), the Mo^{VI} atom has a distorted octahedral geometry (Fig. 1). The $\text{Mo}=\text{O}$ bond lengths and $\text{O1}=\text{Mo}=\text{O2}$ bond angle (Table 1) have values typical for *cis*- MoO_2^{2+} groups. The two types of phenolic C—O bond lengths [mean values 1.332 (2) and 1.352 (2) \AA] of the 2,3-DHBA ligands compare well with those observed for the catecholate (fully reduced) form of the ligand (Buchanan & Pierpont, 1980). The difference in the distances is attributed to the intramolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond (Table 2).

In the packing diagram (Fig. 2), it is important to notice that the large tetraphenylphosphonium ions bring only two molybdenum complex ions into relative proximity. Moreover, no π - π interactions are observed, even though there are a number of benzene rings in both the ligands and the tetra-

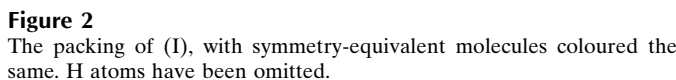


The cyclic voltammograph of (I) in dichloromethane confirmed its catecholate form, showing only a two-electron redox peak corresponding to the catechol-to-quinone oxidation of the ligand. The *cis*-MoO₂²⁺ group can also contain a pentavalent molybdenum ion (Lu *et al.*, 2001), but in the voltammograph no peak due to the Mo^V-to-Mo^{VI} conversion was observed.

All reagents were purchased from Aldrich. An aqueous solution (10.0 ml) of 2,3-DHBA (77.1 mg, 0.5 mmol) and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (121.0 mg, 0.5 mmol) was added to an aqueous solution (12.5 ml) of PPh_4Br (210.0 mg, 0.5 mmol), producing a yellow precipitate. The precipitate (29.1 mg, 0.03 mmol) was dissolved in dichloromethane (15 ml) and, after slow evaporation, crystals of (I) were obtained. Analysis calculated for $\text{C}_{62}\text{H}_{48}\text{O}_{10}\text{P}_2\text{Mo}$: C 66.90, H 4.35%; found C 66.82, H 4.27%.

$(\text{C}_{24}\text{H}_{20}\text{P})_2[\text{Mo}(\text{C}_7\text{H}_4\text{O}_4)_2\text{O}_2]$	Mo $K\alpha$ radiation
$M_r = 1110.88$	Cell parameters from 8839 reflections
Orthorhombic, $Pbca$	$\theta = 2-28.5^\circ$
$a = 13.3595$ (3) Å	$\mu = 0.38 \text{ mm}^{-1}$
$b = 16.9998$ (4) Å	$T = 150$ (2) K
$c = 45.5887$ (13) Å	Block, yellow
$V = 10353.6$ (4) Å ³	$0.60 \times 0.54 \times 0.35 \text{ mm}$
$Z = 8$	
$D_x = 1.425 \text{ Mg m}^{-3}$	

Bruker SMART APEX CCD area-	15149 independent reflections
detector diffractometer	11301 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.058$
Absorption correction: multi-scan	$\theta_{\text{max}} = 30.1^\circ$
(<i>SADABS</i> ; Sheldrick, 2004)	$h = -18 \rightarrow 18$
$T_{\text{min}} = 0.732$, $T_{\text{max}} = 0.880$	$k = -23 \rightarrow 23$
122211 measured reflections	$l = -64 \rightarrow 63$



Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.100$
 $S = 1.06$
 15149 reflections
 678 parameters
 H-atom parameters constrained

$$\begin{aligned} w &= 1/[\sigma^2(F_o^2) + (0.0315P)^2 \\ &\quad + 9.6314P] \\ \text{where } P &= (F_o^2 + 2F_c^2)/3 \\ (\Delta/\sigma)_{\max} &= 0.002 \\ \Delta\rho_{\max} &= 0.48 \text{ e } \text{\AA}^{-3} \\ \Delta\rho_{\min} &= -0.50 \text{ e } \text{\AA}^{-3} \end{aligned}$$

Mo1—O1	1.7056 (15)	O12—C22	1.331 (2)
Mo1—O2	1.7151 (15)	C71—O81	1.349 (2)
Mo1—O81	1.9765 (14)	C72—O82	1.355 (2)
Mo1—O82	1.9865 (14)	C91—O911	1.217 (3)
Mo1—O12	2.2198 (14)	C91—O912	1.340 (3)
Mo1—O11	2.2255 (14)	C92—O921	1.218 (3)
O11—C21	1.332 (2)	C92—O922	1.344 (3)
O1—Mo1—O2	103.36 (7)	O1—Mo1—O11	88.97 (6)
O1—Mo1—O81	105.89 (7)	O2—Mo1—O11	164.19 (7)
O2—Mo1—O81	91.32 (7)	O81—Mo1—O11	75.61 (5)
O1—Mo1—O82	92.12 (7)	O82—Mo1—O11	85.53 (5)
O2—Mo1—O82	103.59 (7)	O12—Mo1—O11	77.43 (5)
O81—Mo1—O82	153.40 (6)	C21—O11—Mo1	111.89 (12)
O1—Mo1—O12	161.83 (7)	C22—O12—Mo1	113.07 (12)
O2—Mo1—O12	92.29 (6)	C71—O81—Mo1	120.06 (12)
O81—Mo1—O12	82.58 (6)	C72—O82—Mo1	120.75 (12)
O82—Mo1—O12	75.03 (5)		

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O912—H912...O11	0.84	1.73	2.514 (2)	155
O922—H922...O12	0.84	1.74	2.523 (2)	155
C33—H33...O912 ⁱ	0.95	2.54	3.357 (3)	144
C43—H43...O911 ⁱ	0.95	2.29	3.178 (3)	154
C44—H44...O2 ⁱⁱ	0.95	2.48	3.195 (3)	132
C54—H54...O911 ⁱ	0.95	2.55	3.249 (3)	131
C163—H163...O12 ⁱⁱⁱ	0.95	2.46	3.348 (3)	156
C173—H173...O922 ⁱⁱⁱ	0.95	2.58	3.370 (3)	141
C223—H223...O921 ^{iv}	0.95	2.55	3.447 (3)	158
C233—H233...O922 ^{iv}	0.95	2.53	3.310 (3)	140

The hydroxyl H atoms were located in difference maps and the OH groups were subsequently refined as rotating rigid groups, with $\text{O}-\text{H} = 0.84 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$. Other H atoms were placed in calculated positions, with $\text{C}-\text{H} = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Siemens, 1993); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1996); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1997); software used to prepare material for publication: *XCIF* (Sheldrick, 1993) and *PLATON* (Spek, 2003).

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